P H Y S I C A L   R E V I E W   L E T T E R S

Equation of State Beyond the Radius of Convergence of the Virial Expansion

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The well-known problem of the virial expansion low-density limitation is considered within Mayer's cluster expansion method. The expression for the configuration integral and the corresponding equation of state are presented based on this approach but not limited by the convergence radius of the series for density and activity. When taking into account any number of irreducible integrals at the thermodynamic limit, this equation of state demonstrates the exact coincidence with the virial one inside the domain of its convergence but specifies the condensation process directly outside that domain. Thus, the assumption of some researchers that the condensation should appear in the domain where the proof of the virial expansion is limited may now be regarded as confirmed, exclusively using the classical Gibbs statistics.

At present, there is no rigorous theory of phase transitions based on the statistical approach considering only an interaction potential without any additional assumptions. In the first half of the 20th century, J. Mayer [1] offered the method of the cluster expansion of the configuration integral. The virial equation of state derived by this method is considered to be the only one that has been strictly theoretically proved. It has been shown by J. Mayer that the virial coefficients B_{k+1} of this equation are directly related to the corresponding irreducible integrals β_k [the integral of the product of Mayer's functions over the configuration space of $(k + 1)$ molecules that cannot be expressed by the products of lower-order integrals]

$$B_{k+1} = -\frac{k}{k+1}\beta_k.$$

Unfortunately, Mayer's proof of the virial equation has a strong limitation for the particle number density ρ

$$\sum_k k\beta_k\rho^k < 1 \qquad (1)$$

related to the radius of convergence of the power series for density and activity. Correspondingly, all attempts to determine the point of condensation or even to prove its existence using the Gibbs statistical approach, exclusively, have failed [2]. The researchers could only suppose that phase transitions would occur at this domain [3,4].

The Kadanoff-Wilson-Fisher renormalization group approach [5,6] based on the Gibbs statistics [7] has been considered a noticeable success in the theory of critical phenomena for a wide range of physical processes, but it is not applicable to describe the first-order phase transitions and contains some additional assumptions and hypotheses [8] that have not been proven theoretically.

Another conventional approach based on the Ornstein-Zernike (OZ) equation [9] has led to some success in the description of the first-order phase transitions [10] as well as the critical phenomena [11,12]. The OZ equation is

actually a simplification of the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy and equivalent to the Gibbs statistics [13] but requires some additional equation, known as the closure relation. Widely used, the Percus-Yevick [14], hypernetted-chain [15], and Martynov-Sarkisov [16] closures are approximations rather than strictly proven equations. Moreover, it was shown in Refs. [10,11] that, in principle, the OZ equation should have no solution for the domain of condensation.

In any case, the coincidence of the domain of the virial expansion divergence with the condensation domain [3,4,10,11] has remained an assumption, and the conventional opinion has been that the classical (Gibbs) statistical approach is unable to describe the phase transitions of matter.

Therefore, there is the question if the convergence condition of the virial equation does really limit the Gibbs statistical approach, in general, as well as the cluster expansion of Mayer, in particular, or in other words, whether it is possible to establish the expressions of the configuration integral and equation of state not limited by condition (1).

In the cluster expansion [1], the configuration integral Q_N is expressed by the cluster integrals of b_j

$$Q_N = V^N N! \sum_{\{m_j\}} \prod_{j=1}^{N} \frac{b_j^{m_j}}{m_j!}, \qquad (2)$$

where $\{m_j\}$ is a sequence of N positive integers that satisfies the condition

$$\sum_{j=1}^{N} jm_j = N. \qquad (2a)$$

In turn, any of the cluster integrals is expressed by the irreducible integrals of β_k

$$b_j = j^{-2} \sum_{\{n_k\}} \prod_{k=1}^{j-1} \frac{1}{n_k!} \left(j\frac{\beta_k}{V^k}\right)^{n_k}, \qquad (3)$$

where $\{n_k\}$ is a set of $(j-1)$ positive integers that satisfies the condition

$$\sum_{k=1}^{j-1} k n_k = j - 1. \tag{3a}$$

Expressions (2) and (3) are very complex to analyze and practically use, even for modern computing technologies. However, in Ref. [17] the numerical investigations based on Eqs. (2) and (3) were carried out in the simplified case (only taking into account the first irreducible integral, i.e., the second virial coefficient) for the limited number of particles (up to $N = 1500$) that showed significant differences in comparison with the virial expansion at high densities.

To obtain the expression of the configuration integral in a more convenient form for the analysis, J. Mayer suggested considering expressions (2) and (3) as the coefficients in the power expansion of certain functions [1].

A similar approach {see Supplemental Material for "Derivation of function (4)" [18]} leads to the conclusion that the value $Q_N/(V^N N!)$ is exactly the coefficient at y^N in the power expansion of the following function

$$F(y) = \left(1 - \sum_{k \geq 1} k \frac{\beta_k}{V^k} y^k\right) \exp\left(y\left[1 - \sum_{k \geq 1} \frac{k}{k+1} \frac{\beta_k}{V^k} y^k\right] + N \sum_{k \geq 1} \frac{\beta_k}{V^k} y^k\right). \tag{4}$$

Considering the Taylor series of function (4), we can obtain the expression of the configuration integral

$$Q_N = V^N q_N, \tag{5}$$

where

$$q_N = \left(\frac{\partial^N F(y)}{\partial y^N}\right)_{y=0} = M_N - \sum_{k=1}^{N} \frac{N!}{(N-k)!} k \frac{\beta_k \rho^k}{N^k} M_{N-k}, \tag{6}$$

and the values of M_k are defined in the following recursive expression

$$M_k = M_{k-1} + \sum_{i=1}^{k} \frac{i \beta_i \rho^i}{N^{i-1}} \frac{(k-1)!}{(k-i)!}\left[M_{k-i} - \frac{(k-i)}{N} M_{k-1-i}\right], \tag{7}$$

while $M_0 = 1$ and $M_{k<0} = 0$.

Equation (5), taking into account Eqs. (6) and (7), gives exactly the same results as expressions (2) and (3) without any restrictions on ρ, but it is considerably more convenient to study and allows derivation of the equation of state

$$\frac{PV}{NkT} = \frac{q_{N-1} - \sum_{k=1}^{N-1} \frac{k}{k+1} \frac{\beta_k \rho^k}{N^k} \frac{(N-1)!}{(N-1-k)!} q_{N-1-k}}{q_N}. \tag{8}$$

The virial equation in the form obtained by J. Mayer

$$\frac{PV}{NkT} = 1 - \sum_{k \geq 1} \frac{k}{k+1} \beta_k \rho^k \tag{9}$$

is just the simplification of Eq. (8) for $N \to \infty$ and

$$\frac{(N-1)!}{(N-1-k)!} \to N^k$$

in the regime, when $q_n \approx q_i$. Such simplification should be adequate under condition (1), but we do not know whether it is reliable at $\rho \gtrsim \rho_0$, where ρ_0 is the minimum density that violates this condition:

$$\sum_k k \beta_k \rho_0^k = 1. \tag{10}$$

Eliminating the dependence on N from Eq. (8) at the thermodynamic limit ($N \to \infty$) without losing important information is an intricate problem, because the equation includes the combination of both very small and very large values simultaneously. It seems impossible to express recursive relationship (7) (or the corresponding complex polynomials) by simple analytical functions.

On the other hand, the condition of free-energy additivity and thus the proportionality of the configuration integral logarithm to N at the thermodynamic limit allows us to suppose that the polynomials presented by M_k's in Eq. (7) can be considered (with sufficiently large N and k) as the power k of some function $Z(\rho)$.

Let us consider the ratio

$$Z_k = \frac{M_k}{M_{k-1}} = 1 + \sum_{i=1}^{k} \frac{i \beta_i \rho^i}{N^{i-1}} \frac{(k-1)!}{(k-i)!} Y_{k,i}, \tag{11}$$

where

$$Y_{k,i} = \prod_{n=1}^{i-1} \frac{1}{Z_{k-n}} - \frac{(k-i)}{N} \prod_{n=1}^{i} \frac{1}{Z_{k-n}}.$$

At the thermodynamic limit ($N \to \infty$), taking into account the finite number of irreducible integrals ($i \ll N$), supposing

$$\frac{1}{N^i} \frac{N!}{(N-i)!} \to 1$$

and $Z_{N-i} \approx Z_N \approx Z$, we would establish that the function $Z(\rho)$ is one of the roots of the equation

$$Z = 1 + (Z - 1) \sum_{k \geq 1} \frac{k \beta_k \rho^k}{Z^k}, \tag{12}$$

and equation of state (8) acquires the form

$$\frac{PV}{NkT} = \frac{1 - \sum_{k \geq 1} \frac{k}{k+1} \beta_k (\frac{\rho}{Z})^k}{Z}. \tag{13}$$
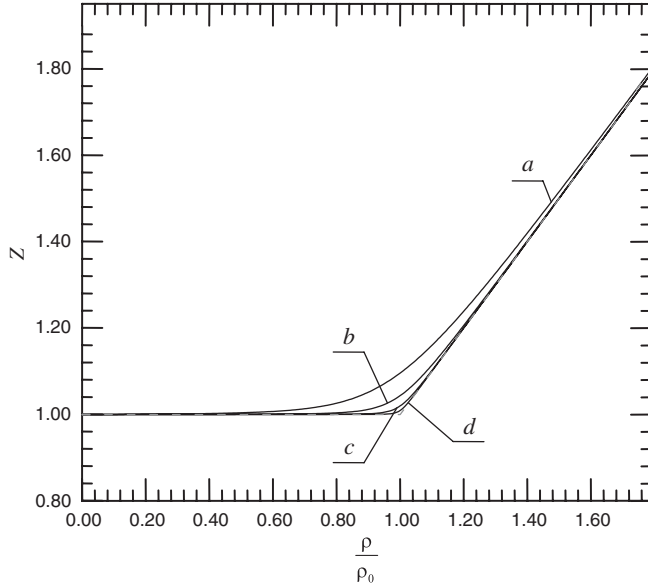
One of the roots of Eq. (12) is obvious as

$$Z = 1,$$

FIG. 1.   Dependence Z_N in Eq. (11) on ρ for different particle numbers [the dashed line shows function (15)]: a, $N = 500$; b, $N = 5000$; c, $N = 50\,000$; d, $N = 500\,000$.

and the others ($Z \neq 1$) are defined by the equation

$$\sum_{k \geq 1} k \beta_k \left(\frac{\rho}{Z}\right)^k = 1. \tag{14}$$

As Mayer's proof of the virial expansion at limitation (1) is valid, the only possible value of Z in the corresponding states (low density or high temperature) should be 1 [Eq. (13) is transformed to Eq. (9)].

Let us consider $Z(\rho)$ in detail at some temperatures (below critical) where the set of irreducible integrals at low density ($\rho < \rho_0$) satisfies condition (1) (so that $Z = 1$), but at higher density ($\rho > \rho_0$) violates this condition. In the latter regime, the set of M_k values in Eq. (7) forms a strictly increasing sequence {see Supplemental Material for "Increasing of the sequence of M_k's in Eq. (7)" [18]}, and $Z(\rho)$ must be defined by Eq. (14); i.e., it is proportional to the density. The behavior described,

$$Z(\rho) = \begin{cases} 1; & \rho \leq \rho_0 \\ \rho/\rho_0; & \rho > \rho_0, \end{cases} \tag{15}$$

is illustrated in Fig. 1. There are a number of computational plots of Z_N from Eq. (11) for different particle numbers N in this figure to compare with Eq. (15).

When N is increasing, the plots of Z_N really converge to function (15). Moreover, the plots are independent of both the values and the number of irreducible integrals taken into account—the dependence is encapsulated in ρ_0 (the set of integrals should meet one criterion—the existence of real positive ρ_0; i.e. they should correspond to the temperatures below critical).
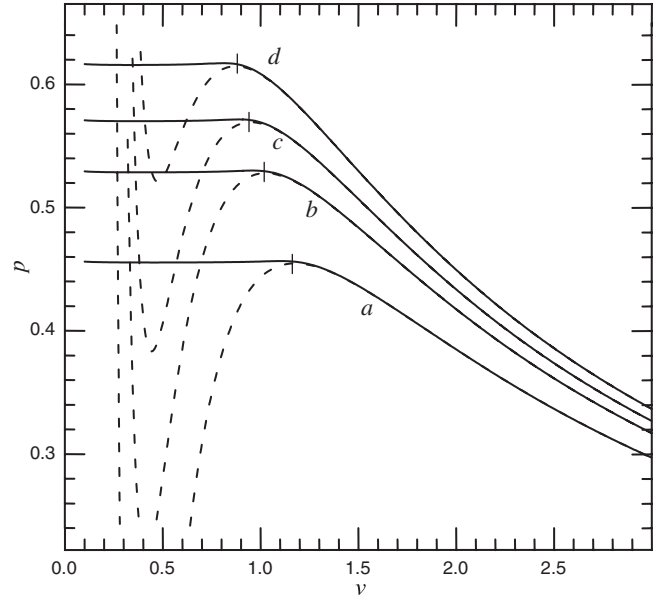

FIG. 2.   Isotherms of Eq. (16) (solid lines) and virial Eq. (9) (dashed lines) of the Lennard-Jones system for different temperatures: a, $\tau = 1.15$; b, $\tau = 1.2$; c, $\tau = 1.225$; d, $\tau = 1.25$.

Substituting function (15) into Eq. (13), we finally obtain the following piecewise equation of state

$$\frac{P}{kT} = \begin{cases} \rho\left(1 - \sum_{k \geq 1} \frac{k}{k+1} \beta_k \rho^k\right); & \rho \leq \rho_0 \\ \rho_0\left(1 - \sum_{k \geq 1} \frac{k}{k+1} \beta_k \rho_0^k\right); & \rho > \rho_0, \end{cases} \tag{16}$$

where ρ_0 is defined as the minimum real positive root of Eq. (10).

Figure 2 illustrates the behavior of Eq. (16) in comparison with the virial equation of state taking into account irreducible integrals up to the third order, inclusive (i.e., the second, third, and fourth virial coefficients), for the Lennard-Jones (12-6) potential. In order to eliminate the dependence on the parameters D and ε_0 of this potential (equilibrium distance between a pair of molecules and dissociation energy, respectively), the equations of state were transformed to more general form for dimensionless pressure $p = P/P_0$, volume $v = V/V_0$, and temperature $\tau = kT/\varepsilon_0$, where $P_0 = \varepsilon_0/b$, $V_0 = Nb$, and $b = \frac{4}{3}\pi D^3$. There is a vertical marker on each isotherm corresponding to ρ_0, where condition (1) is violated.

The convergence of plots $P(V)$ from Eq. (8) to Eq. (16) for sufficiently large N is demonstrated in Fig. 3. The behavior of Eq. (16) at $\rho \geq \rho_0$ demonstrates the process of condensation while the value ρ_0 is the same as the dry saturated vapor density.

Thus, within the scope of the Gibbs statistics using Mayer's cluster expansion without any additional assumptions, it is possible to establish equations for the domain of state where the conventional virial expansion is not
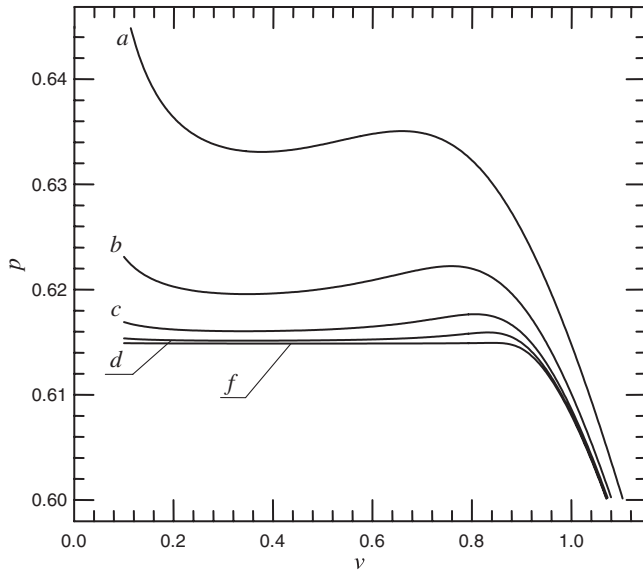
FIG. 3.   Isotherms ($\tau = 1.25$) of Eq. (8) of the Lennard-Jones system for different numbers of particles: a, $N = 500$; b, $N = 2000$; c, $N = 8000$; d, $N = 32\,000$; f, $N = 120\,000$.

applicable. The behavior of these equations in that domain directly specifies the phase transition.

The assumption [3,4] that the condensation occurs in the virial expansion divergence domain may now be regarded as proved. Therefore, we should consider as strict all the relationships between the irreducible integrals (virial coefficients) and the condensation parameters (as well as the critical parameters) based on Eq. (10) [10,11].

It is important to note the fact that the condensation which was ''elusive'' with earlier statistical approaches, really, is an inherent property of the cluster expansion series (or any other series of similar type) and appears when we take into account any number of irreducible integrals (even the only one two-body integral) as well as using any type of the interaction potential capable of producing real positive roots of Eq. (10).

On the other hand, it would be incorrect to assert that the condensation considered in this Letter is absolutely adequate to the real process—the equations only describe its beginning but do not describe the boiling point and the liquid state. As ρ is increasing, the sum in condition (1) is changing nonlinearly and this condition may be even satisfied at $\rho > \rho_0$. However, in this regime both the proof of the virial equation and Eq. (16) cannot be considered strict.

Equation (16) has been obtained using some approximations [see the derivation of Eq. (12)] which require one to take the finite number k ($k \ll N$) of irreducible integrals into account while $N \to \infty$. All the numerical calculations for small k and large N values demonstrate the constancy of pressure wherever density exceeds the dew point density. Apparently, an accurate description of repulsive forces (i.e., the property of the configuration integral to approach zero at high densities) requires one to take all actual ($k = N - 1$) integrals into account; that is, unfortunately, impossible, not only at the thermodynamic limit ($N \to \infty$) but even for large N values.

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